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Liquid Crystalline Phases and Emulsifying Properties of Block Copolymer Hydrophobic Aliphatic and Hydrophilic Peptidic Chains

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Amphiphilic lipopeptides with a hydrophobic paraffinic chain containing from 12 to 18 carbon atoms and a hydrophilic peptidic chain exhibit lyotropic mesophases and good emulsifying properties. The X-ray diffraction study of the mesophases and of dry lipopeptides showed the existence of three types of mesomorphic structures : lamellar, cylindrical hexagonal and body-centred cubic. Two types of polymorphism were also identified : one as a function of the length of the peptidic chain and the other as a function of the water content of the mesophases. The emulsifying properties of the lipopeptides in numerous pairs of immiscible liquids such as water/ hydrocarbons and water/base products of the cosmetic industry showed that small amounts of lipopeptides easily give three types of emulsions : simple emulsions, miniemulsions and microemulsions.

Many surfactants have been used to formulate microemulsions (1). They were of three types : anionic surfactants such as petroleum sulfonates, sodium octyl benzene sulfonate, sodium dodecyl sulfate, alkaline soaps ; cationic surfactants such as dodecyl ammonium and hexadecyl ammonium chlorides or bromides ; and nonionic surfactants such as polyoxyethylene glycols. Furthermore, many exhibit liquid-crystalline properties (2) and in some cases the structure of the mesophases has been established (3). Nevertheless, nearly nothing is known about their compatibility with blood and tissues, and, from our own experience, some exhibit a high lytic power for red cells (4).

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In order to obtain surfactants able to emulsify base products for cosmetic industry without presenting adverse side effects to the skin and tissues, it was necessary to synthesize new surfactants. We have chosen as new surfactants the amphiphilic lipopeptides (5-6).

Amphiphilic lipopeptides $C_n(AA)_p$ are formed by a hydrophobic lipidic chain C_n containing from 12 to 18 carbon atoms linked through an amide bond to a hydrophilic peptidic chain $(AA)_p$ with a number average degree of polymerization p between 1 and 90. The repeating unit of the peptidic chain is an amino-acid residue and the general formula of the lipopeptides $Cn(AA)_p$ is :

$$H-(CH_2)_n-NH-(CO-\underset{R}{CH}-\underset{R'}{N})_p-H$$
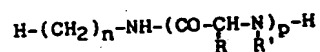
with R' = H (except for sarcosine where R' = CH_3) and R is the side chain of the amino-acid. The following are the various amino-acid residues : sarcosine (Sar) with R = H ; lysine bromhydrate (K) with R = $(CH_2)_4-NH_2$,HBr ; sodium salt of glutamic acid (E) with R = $(CH_2)_2-COONa$; hydroxyethylglutamine (Eet) with R = $(CH_2)_2-CO-NH-(CH_2)_2OH$ and hydroxypropylglutamine (Epro) with R = $(CH_2)_2-CO-NH-(CH_2)_3OH$.

Lipopeptides present three main advantages. The two parts of the lipopeptide molecules (lipidic and peptidic chains) are present in many biological molecules and macromolecules and one can expect a good compatibility with biological fluids and tissues (4) and an absence of toxicity of their degradation products. The HLB of lipopeptides can be easily adjusted by varying the degree of polymerization p of the peptidic chains and the nature of the amino-acid side chains R. The incompatibility between the hydrophobic paraffinic chains and the hydrophilic peptidic chains leads to a phase separation at the molecular scale and to the existence of mesophases (7).

In this paper, we will describe the lyotropic liquid crystalline and the emulsifying properties of lipopeptides with peptidic chains.

EXPERIMENTAL METHODS

Preparation of Mesophases. Lipopeptides are dissolved in a small excess of water and, when total homogeneity is achieved, the desired concentration is obtained by slow evaporation at room temperature. Then the sample is left at room temperature in tight cells to reach equilibrium.

X-ray Diffraction Studies. They are performed under vacuum with a Guinier type focussing camera equipped with a bent quartz monochromator giving a linear collimation of the $CuK_{\alpha 1}$ (λ = 1.54 Å) radiation (8).

Preparation of Emulsions. The mixture oil-lipopeptide is heated to 70°C under agitation for complete homogeneization. It is then cooled to 45°C and water is added. The agitation is maintained throughout the preparation and until the system is cooled to room temperature (9).

Preparation of Miniemulsions. They are prepared by two methods :

  - In the first method, the ionic lipopeptide and cetyl alcohol
are mixed with water for an hour at 63°C (pre-emulsification stage).
The oil is then added at 63°C and the agitation is continued for an
additional hour (9,10).
  - In the second method, the mixture oil/lipopeptide/cetyl alco-
hol is homogeneized at 70°C for several minutes ; then it is cooled
at 50°C and water is added, agitation is carried on until complete
homogeneization. The system is then cooled to room temperature under
agitation (9).

Preparation of Microemulsions. Oil, lipopeptide and water are mixed
in the same way as in emulsion preparation ; the mixture is then
titrated, at room temperature, with the cosurfactant until transpa-
rency is obtained (9).

Stability of Emulsions and Miniemulsions. The stability of emulsions
and miniemulsions is determined by following, as a function of time,
the variation of the emulsified volume at fixed temperatures between
- 10°C and + 50°C.

RESULTS AND DISCUSSION

Liquid-Crystalline Properties

Structure and Polymorphism of Lipopeptides. Amphiphilic lipopep-
tides $C_n(AA)_p$ exhibit mesophases in aqueous solution for water
concentrations smaller than about 60 %. The structure of the meso-
phases and of the dry lipopeptides obtained by evaporation of the
mesophase water at a slow rate was determined by X-ray diffraction.
Lipopeptides X-ray diagrams obtained are similar to those exhibited
by classical amphiphiles (11). They have allowed us to establish the
existence of three types of liquid-crystalline structures : lamel-
lar, hexagonal and cubic.
  The lamellar structure consists of plane, parallel equidistant
sheets ; each sheet of thickness d results from the superposition of
two layers : one of thickness d_A contains the hydrophilic peptidic
chains and the water, while the other layer of thickness d_B contains
the hydrophobic paraffinic chains.
  The hexagonal structure consists of long and parallel cylinders
of diameter $2R_H$, filled with the hydrophobic paraffinic chains of
the lipopeptides and assembled in a hexagonal array of parameter D,
while the space between the cylinders is occupied by the hydrophilic
peptidic chains and the water.
  The body-centred cubic structure consists of spheres of diame-
ter $2R_C$ filled with the hydrophobic paraffinic chains of lipopep-
tides and assembled on a body centred cubic lattice of side a, while
the space between the spheres is occupied by the hydrophilic pepti-
dic chains and the water.
  The lattice parameters d, D and a are directly obtained from X-
ray patterns, while the other parameters : d_A, d_B, 2R and S (average
surface occupied by a chain at the interface between the hydrophilic
and hydrophobic domains) are calculated using formulae based on
simple geometrical considerations (11,12).
  The type of structure adopted by the lipopeptides is determined
by the ratio of the volumes of the hydrophilic domains (containing

the peptidic chains and the water) and the hydrophobic domains (containing the paraffinic chains). Therefore the lipopeptides exhibit two types of polymorphism : one as a function of the length of the peptidic chains and the other as a function of the water content of the mesophases. When the degree of polymerization p of the peptidic chains increases dry lipopeptides (obtained by evaporation of the water) exhibit successively lamellar, hexagonal and cubic structures in the case of liposarcosine (12) and lamellar and hexagonal structure in the case of lipolysine and lipo(glutamic acid) (13). Furthermore the addition of water to lipopeptides is able to transform the lamellar structure into a hexagonal one (12-13) or a hexagonal structure into a body-centred cubic one (12).

Factors Governing the Geometrical Parameters of the Mesophase. The factors governing the geometrical parameters of the liquid-crystalline structures are the water content of the mesophases, the length of the paraffinic chains and the length of the peptidic chains.

   Influence of the Water Concentration. When the water concentration increases :

   - The lattice parameter : d for the lamellar structure, D for the hexagonal structure and a for the cubic structure increases.

   - The characteristic parameter of the hydrophobic domains : d_B for the lamellar structure, $2R_H$ for the hexagonal structure and $2R_C$ for the cubic structure decreases.

   - The characteristic parameter of the hydrophilic domains : d_A for the lamellar structure, $D-2R_H$ for the hexagonal structure and $a-2R_C$ for the cubic structure increases.

   - The average surface S available for a molecule at the interface increases for the 3 types of structure.

   The figures 1 and 2 illustrate such a behaviour in the case of the lamellar and hexagonal structures of $C_{18}K_2$, and of the body-centred cubic structure of $C_{17}Sar_{50}$ respectively.

   Influence of the Length of the Paraffinic Chains. Sets of lipopeptides $C_n(AA)_p$, with the same degree of polymerization p for the peptidic chains, but with a number of carbon atoms n of their paraffinic chains equal to 12, 14, 16, 17 and 18 have been studied. When the number n of carbon atoms increases, d, D, d_B and $2R_H$ increase, while the characteristic parameter of the hydrophilic peptidic domains and S both remain constant (9,12).

   Influence of the Length of the Peptidic Chains. Three sets of lipopeptides $C_{17}Sar_p$, $C_{18}K_p$ and $C_{18}E_p$ with a constant length of the paraffinic chains and different values of the degree of polymerization p of the peptidic chains have been studied. For the 3 types of structures (lamellar, hexagonal and body-centred cubic) when p increases the lattice parameter, the characteristic parameter of the hydrophilic peptidic chains and the specific surface all increase. The characteristic parameter of the hydrophobic paraffinic chains decreases (12,13).

Emulsifying Properties

The emulsifying properties of lipopeptides were tested in many oil/water systems. The oil was aromatic such as toluene and styrene, paraffinic such as decane and dodecane, or a base product of the cosmetic industry. Lipopeptides give 3 types of emulsions : macro-
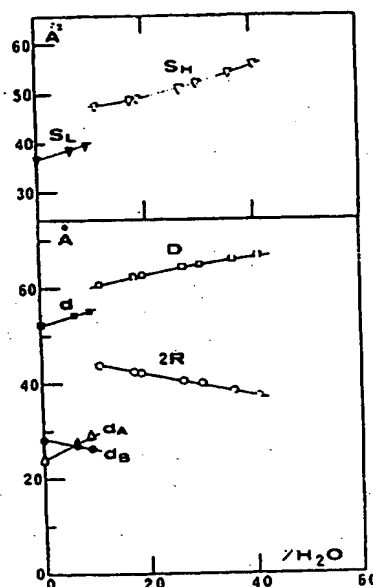
Figure 1. Variation of the parameters of the lamellar and hexa-gonal structures of lipopeptide $C_{18}K_2$ versus water concentration.
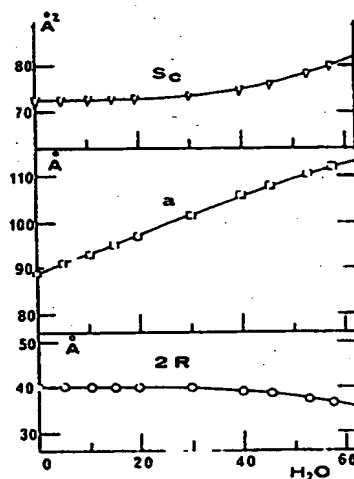

Figure 2. Variation of the parameters of the body-centered cubic structure of lipopeptide $C_{17}Sar_{50}$ versus water concentration.

emulsions with droplet diameters higher than 1000 nm, miniemulsions with droplet diameters between 100 and 400 nm, and microemulsions with droplet diameters between 10 and 100 nm. We will sum up the main results obtained with the 3 types of emulsions.

Type of Emulsions. The emulsions vary from a fluid milklike to a thick cream, depending upon the nature of the oil, the ratio oil/water, the nature and the concentration of the lipopeptides.
     All the emulsions are of the oil in water (O/W) type as shown by the dilution method, the selective dyes method and the conductivity method (9). Such a result is in agreement with the HLB values (between 8 and 15) of the lipopeptides (9).

Stability of Emulsions. Stabilities varying from 2 months to more than 24 months were found.
     The main factors governing the stability of the emulsions are : the length of the paraffinic chains, the nature, the degree of polymerization and the end group of the peptidic chain and the nature of the oil.
     Influence of the Length of the Paraffinic Chains. The comparative study of lipopeptides with the same peptidic chains but with paraffinic chains containing from 12 to 18 carbon atoms has shown that emulsions obtained with lipopeptides with a paraffinic chain containing 12 or 14 carbon atoms are stable for less than 4 days. Emulsions obtained using lipopeptides with paraffinic chains containing 16 or 18 carbon atoms are stable for longer than 3 months. Nevertheless, the domain of stability of the emulsions is slightly higher for the 18 carbon atoms paraffinic chains than for the 16.
     C_{12} and C_{14} lipopeptides are more soluble in water than their C_{16} and C_{18} counterparts and can be more easily carried into the aqueous phase destroying the hydrophilic-hydrophobic equilibrium between the lipopeptides and the water and oil phases.
     Influence of the Peptidic Chain End Group. The influence of the nature of the peptidic chain end group has been studied for 4 types of lipopeptides : liposarcosine, lipolysinebromhydrate, lipoglutamic acid sodium salt and lipohydroxyethylglutamine ; similar results were obtained.
     Figure 3 illustrates the results obtained in the emulsification of the O/W isopropyl myristate/water system by a liposarcosine with a degree of polymerization of 2 and a 18 carbon atoms paraffinic chain. The domain of stability of the emulsions decreases from the liposarcosine chlorhydrate (dotted line), to the liposarcosine (full line) and to the liposarcosine whose terminal amine function has been acetylated (points).
     When the polarity of the end group of the peptidic chain decreases, the emulsifying power of the lipopeptide decreases.
     Influence of the Nature of the Amino-acid Side Chain. The influence of the nature of the amino-acid side chain on the emulsifying properties of lipopeptides is illustrated in the figure 4 for the system O/W isopropyl myristate/water, and for 4 lipopeptides with a paraffinic chain containing 18 carbon atoms and with a degree of polymerization of 2 for the peptidic chains. The emulsions stability region decreases from lipohydroxyethylglutamine (full line) to lipolysine (dotted line), to lipoglutamic acid (points) and to hydroxypropylglutamine (crosses). This behaviour is related to the
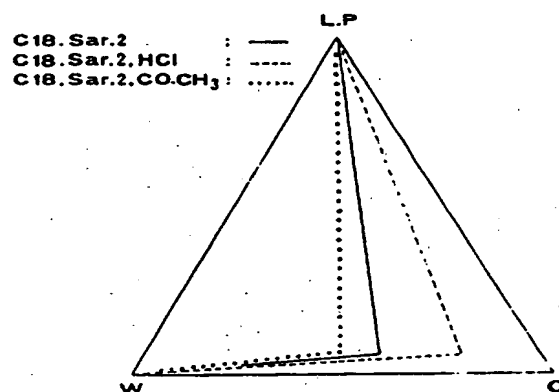
Figure 3. Influence of the nature of the end group of the pepti-
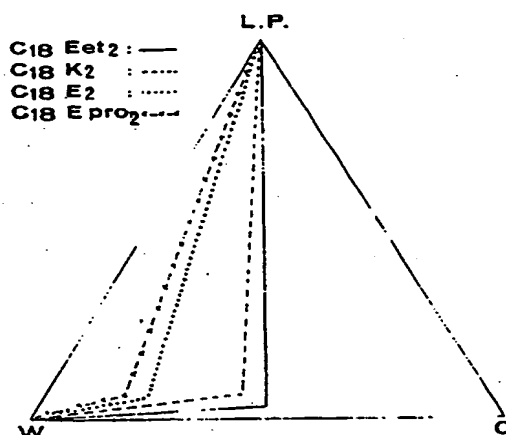dic chains on the domain of stability of emulsions.

Figure 4. Influence of the nature of the amino-acid side chain
on the domain of stability of emulsions.

number of hydrophilic sites per amino-acid residue and to the hydro-
philicity of the amino-acid residue.

For less polar oils such as dodecane similar results were
obtained. The hydrophilicity of the peptidic chain plays an impor-
tant part in the emulsifying properties of lipopeptides for common
oils.

Influence of the Degree of Polymerization of the Peptidic Chain. The
influence of the degree of polymerization p of the peptidic chains
of lipopeptides has been studied for 3 types of lipopeptides :
liposarcosine, lipolysine bromhydrate and lipoglutamic acid sodium
salt with paraffinic chains containing 18 carbon atoms. The degree
of polymerization p of the peptidic chains was between 1 and 10.
Lipopeptides with p ⩾ 5 give emulsions stable for less than 3 days.
Lipopeptides with p = 1, 2 or 3 give stable emulsions. Figure 5
illustrates the results obtained in the case of the system O/W
isopropyl myristate/water and of lipolysine bromhydrates. One can
see that the domain of stability of the emulsions decreases when p
increases from 1 to 3. For lipoglutamic acid sodium salts similar
results were obtained. For liposarcosines, in contrast, the domain
of stability of emulsions is nearly the same for p = 1,2 and 3.

Influence of the Oil Nature. The influence of the oil's nature
on the domain of stability of emulsions O/W has been studied for 3
types of lipopeptides with a paraffinic chain containing 18 carbon
atoms : lipolysine bromhydrate, liposarcosine chlorhydrate and lipo-
sarcosine. The results obtained were similar for the 3 types of
lipopeptides. The figure 6 illustrates the result obtained in the
case of liposarcosine with a degree of polymerization of 2. The
domain of stability of the O/W emulsions decreases from isopropyl
myristate and butyl stearate (full line) to Mygliol (doted line), to
Cosbiol (cross), to dodecane (points) and to styrene. Polar oils are
easier to emulsify than non polar and aromatic ones.

Miniemulsions

Lipopeptides emulsify with difficulty aromatic oils such as styrene
or toluene. Furthermore they are not able to emulsify some oils such
as vaseline, ricin, wheat germ and silicon oils. To emulsify such
oils we have used a binary emulsifying system consisting of a mix-
ture of a fatty alcohol (cetyl alcohol) and a ionic lipopeptide
(liposarcosine chlorhydrate, lipolysine bromhydrate or lipoglutamic
acid sodium salt). With concentrations of lipopeptide and cetyl
alcohol of 1 to 3 % we have obtained miniemulsions similar to those
obtained by El Aasser and al. with sodium lauryl sulfate and cetyl
alcohol (10).

Type of Miniemulsions.   All the miniemulsions were found to be of
the O/W type.

Stability of the Miniemulsions. The main factors governing the
stability of the miniemulsions are : the length of the paraffinic
chains, the nature of the peptidic chains, the degree of polymeriza-
tion of the peptidic chains, the mixed emulsifier concentration, the
molar ratio lipopeptide/cetyl alcohol, the nature of the oil and the
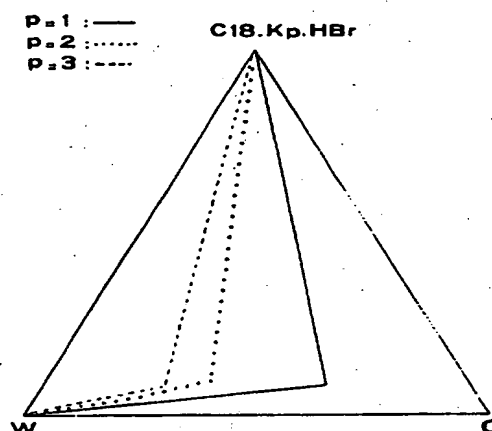method of preparation of the miniemulsions.

p ₌ 1 : ——
p ₌ 2 : ·······
p ₌ 3 : ----

C18.Kp.HBr

W   O

Figure 5.   Influence of the degree of polymerization of the pep-
tidic chains on the domain of stability ef emulsions.

C$_{18}$ Sar$_2$

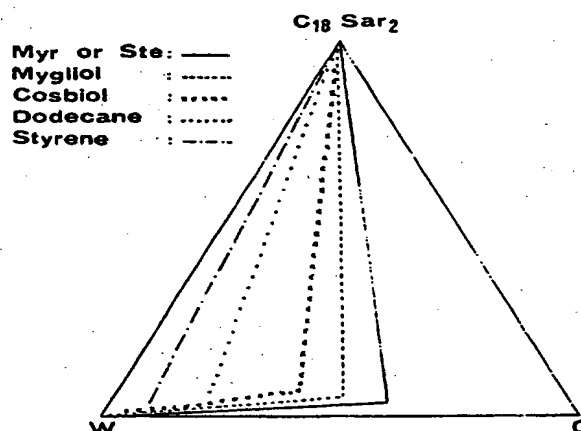Myr or Ste: ——
Mygliol   : -------
Cosbiol   : ······
Dodecane   : ········
Styrene   : —·—··

W   O

Figure 6.   Influence of the nature of the emulsified oil on the
domain of stability of emulsions.

Influence of the Length of the Paraffinic Chains. Lipopeptides with paraffinic chains containing 18 or 16 carbon atoms give with oils very difficult to emulsify (styrene, ricin oil, vaseline oil, silicon oil..) miniemulsions stable for more than 2 months. In contrast, lipopeptides with paraffinic chains containing 14 or 12 carbon atoms give miniemulsions stable for less than 20 days.

Influence of the Nature of the Peptidic Chain. The stability of the miniemulsions decreases when liposarcosine is replaced by lipolysine and lipoglutamic acid. This result is illustrated in Table I for two different oils (styrene and wheat germ oil) for a mass ratio O/O+W of 0.2. Although the amounts of lipopeptide and cetyl alcohol used to obtain miniemulsions have been increased from liposarcosine to lipoglutamic acid and to lipolysine, the stability of the miniemulsions decreases from more than 60 days for liposarcosine, to 12 days for lipolysine and 10 days for lipoglutamic acid.

Table I. Influence of the Nature of the Lipopeptide.

	Styrene			Wheat Germ Oil		
	LP %	$C_{16}OH$ %	Stab.	LP %	$C_{16}OH$ %	Stab.
$C_{18}Sar_2$,HCl	2	1	60	2.5	1.5	60
$C_{18}(K,HBr)_2$	4	1.3	12	4.5	2.0	12
$C_{18}(E,Na)_2$	3	1.2	10	4.0	1.8	10

LP : lipopeptide ; $C_{16}OH$: cetyl alcohol ; Stab.: stability in days.

Influence of the Degree of Polymerization. The amounts of lipopeptide and cetyl alcohol necessary to stabilize miniemulsions increases with the degree of polymerization p of the peptidic chains of lipopeptides. The Table II illustrates this behaviour for the systems styrene/lipolysine bromhydrate and wheat germ oil/lipogluta-mic acid sodium salt.

Table II. Influence of the Degree of Polymerization of the Peptidic Chains.

O/O+W = 0.2		p = 2	p = 3
Styrene	$C_{18}(K,HBr)_p$	4.5 %	7.0 %
	$C_{16}OH$	2.0 %	3.0 %
Wheat germ oil	$C_{12}(E,Na)_p$	4.0 %	6.0 %
	$C_{16}OH$	1.5 %	2.5 %

Influence of the Mixed Emulsifier Concentration. The stability of the miniemulsions increases with the concentration of the mixed emulsifier. Table III illustrates these results for the emulsifi-cation of two different oils : styrene and silicon oil by liposarco-sine chlorhydrate with a degree of polymerization of 2.

Table III. Influence of the Concentration in Weight of Mixed
Emulsifier on the Stability of   Miniemulsions.
LP = $C_{18}Sar_2,HCl$

$\dfrac{O}{O+W}$ = 0.2	$\dfrac{LP}{O+W}$ %	$\dfrac{C_{16}OH}{O+W}$ %	Stability in days
Styrene	2.0 4.0	1.0 2.0	100 > 180
Silicon oil	2.5 5.0	1.5 3.0	70 > 120

Influence of the Molar Ratio Lipopeptide/Cetyl Alcohol. As
already shown by different authors in the case of classical emulsi-
fiers such as sodium lauryl sulfate (10,14,15), the mixed emulsifier
system lipopeptide/cetyl alcohol gives stable miniemulsions for
molar ratios $LP/C_{16}OH$ between 2/1 and 1/3.

Influence of the Ratio Oil/Water. The mass ratio $O/O+W$ cannot
exceed 60 % for aromatic oils and 50 % for cosmetic oils. The
amounts of lipopeptide and cetyl alcohol necessary to obtain minie-
mulsions vary only slightly with the amount of oil in the system
oil/water.

Influence of the Oil Nature. Aromatic oils (toluene and sty-
rene) are easier to miniemulsify than cosmetic oils. They require
smaller amounts of lipopeptide and cetyl alcohol to give stable
miniemulsions.

Influence of the Method of Emulsification. Miniemulsions pre-
pared by the second method are more stable than those prepared with
the preemulsification method.

The Table IV gives 2 examples of the influence of the method of
emulsification on the stability of miniemulsions prepared with the
same amounts of lipopeptide (LP) and cetyl alcohol ($C_{16}OH$). When the
oil is styrene the stability of the miniemulsion increases from 60
to 240 days. When the oil is vaseline oil, the stability of the
miniemulsion increases from 20 to 70 days.

To understand the difference of stability of the miniemulsions
prepared by the two methods we have studied the miniemulsions by
freeze fracture and electron microscopy (9) and measured the size of
the particles. For all the systems studied, the dimensions of the
particles are smaller for the miniemulsions prepared by the second
method ; for instance in the case of styrene (Table IV) the diameter
Ø of the particles is 310 nm against 840 nm. Such a difference in
the particle size explains the difference of stability of the mini-
emulsions prepared by the two methods.

We have also found by freeze fracture and electron microscopy
that the size of the particles increases when the amount of emulsi-
fied oil increases, and decreases when the concentration of the
mixed emulsifier increases. As an example, for the system $C_{18}Sar_2$,
HCl/cetyl alcohol/styrene/water, the average diameter Ø of the par-

ticles increases from 700 nm to 900 nm when the mass ratio O/(O+W) increases from 0.2 to 0.5, but decreases from 900 nm to 750 nm when the surfactant concentration increases from 2 % to 4 %.

Table IV. Influence of the Method of Preparation of Miniemulsion.
$LP = C_{18}Sar_2.HCl$.

O/O+W = 0.2		Method 1	Method 2
Styrene	LP	2 %	2 %
	$C_{16}OH$	1 %	1 %
	Stability	60 days	240 days
	$\emptyset$	840 nm	310 nm
Vaseline oil	LP	2.5 %	2.5 %
	$C_{16}OH$	1.5 %	1.5 %
	Stability	20 days	70 days

Microemulsions

Ionic and nonionic lipopeptides give microemulsions when an aliphatic alcohol or amine with less than 7 carbon atoms is used as cosurfactant. Nevertheless the best cosurfactants are butanol, propanol, butylamine and propylamine.
        The enlargement of the microemulsion region is influenced by the following factors :
        - Increase in the hydrophilicity and HLB of the lipopeptide
        - Decrease of the paraffinic chain length
        - Increase in the polarity of the peptidic chains end group.
        An example is the case of liposarcosine/n-butylamine/isopropylmyristate/water system. Microemulsions region increased from $C_{18}Sar_2$ to $C_{18}Sar_{10}$ as the hydrophilicity of the peptidic chain increased, from $C_{18}Sar_2$ to $C_{18}Sar_2.HCl$ as the polarity of the peptidic chain increased, and from $C_{18}Sar_2.HCl$ to $C_{12}Sar_2.HCl$ as the paraffinic chain length decreased.

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